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Replacement material for natural untanned leather and procedure for its manufacture

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The present invention concerns a new material, namely a replacement for untanned natural leather, as well as a procedure for its manufacture. The new material has properties similar to those of untanned natural leather and this permits the corresponding dressing or finishing under the same conditions. This differentiates it clearly from all other known man-made leather or backings of similar type, intended to receive a dressing by a polyvinyl chloride or polyurethane film.

The new material comprises on the one hand non-woven webs of continuous synthetic fibers obtained by direct thread formation (extrusion). Leather imitation materials manufactured starting with non-woven webs of synthetic fibers are already known. This material is obtained by different methods that are well known in this specialty area and that can be classified into two main groups. The methods of the first group have in common the fact that they are not based on the phenomenon of thermo-retraction – and are hence closer to the procedure of the invention – but lead to materials that have no properties that could compare

to those of natural leather.

In contrast, the methods of the second group are based on thermo-retraction, i.e., on the property of certain synthetic fibers to contract under the effects of a thermal treatment. This phenomenon is also called thermal shrinkage or heat

shrinkage. In principle these methods consist in forming a non-woven web starting from at least one thermally shrinking fiber, needling this web to form a random-fiber fleece of fibers or threads, then subjecting the web in a sequence chosen in accordance with the procedure selected, to thermal shrinkage and impregnation with a synthetic elastomeric bonding agent.

Depending on the sequence chosen for both operational steps, we differentiate a first method, in which thermal shrinkage precedes impregnation. Since shrinkage is accomplished preferably by one or more passes of the web through boiling water, this method has a first disadvantage in requiring an additional step; however, overall it is affected by a more weighty disadvantage, because of the difficulty in evenly distributing the elastomer in the shrunk web, when impregnation is to be carried out afterwards.

In a second method the sequence of the operational steps is reversed, with impregnation preceding thermal shrinkage. However, in the course of shrinking the fiber in part separates from the coagulated elastomeric bonding agent, such that the latter can no longer guarantee complete adhesion between the fibers; this leads to a considerable impairment in the mechanical qualities of the material

and the corresponding limitation in its possible applications.

According to a third method, the procedures are similar for impregnation and heat shrinking, with the latter performed *in situ* in the impregnation bath. This method undoubtedly avoids the disadvantages of the two preceding methods, but it requires using the synthetic elastomers in a hot solvent medium, with all the dangers and disadvantages that result from using organic solvents, especially when hot.

Another method, different from those mentioned above, has already been proposed; it consists in manufacturing a non-woven web starting from two polymers, of which only one is soluble in the organic solvent used and subsequently to eliminate this soluble polymer by treatment of the web in this solvent. It is thus possible to create a porous structure in the end material; however, this method requires the utilization of two polymers and in addition, accepting the disadvantages necessarily entailed in treatments involving the assistance of organic solvents.

Even though it is possible to achieve certain properties of natural leather with the last material mentioned – such as porosity, flexibility and mechanical strength – to date it has not been possible to achieve one property, namely the property of natural leather of swelling in an aqueous medium as soon as a covering layer is in place, thus preventing a too strong or too deep penetration of this layer.

Because this property is lacking in all synthetic leathers and related supports proposed to date, all these materials must be subjected to a dressing with

polyvinyl chloride films or polyurethane films. This dressing can also be realized by using the product in the form of a thickened solution, but then too deep a penetration of the dressing resin must be accepted. In fact, only those materials that are obtained by thermo-retraction, or by impregnation under thermo-sensitization, or in organic solvents, have proven to be satisfactory in this variant of dressing.

A material was now found that is in particular characterized by its ability to swell again in aqueous media, thus remarkably imitating the equally necessary and as yet not realized property of untanned natural leather. The material according to the invention comprises, for instance, a dispersible filler and a synthetic elastomeric latex that constitutes the bonding agent for a non-woven, needled web of continuous synthetic fibers, arranged in the web without any preferred orientation. It is characterized by the dispersible filler being hydrophobic, the needled web being formed of threads with a titer between 0.5 and 10 dtex, where the value can be identical or different; by the bonding agent mixture containing, among other things, a swelling agent that after drying can swell again in an aqueous medium; and be the bonding agent being so distributed inside the web that its density increases from the left or back side towards the right or front side, where this composition and this structure endow the material with properties that are similar to those of untanned natural leather, allowing the dressing destined for the latter, in particular the covering color dressing with the napping board and with a spray gun, using emulsion products.

This new material is very different from current split or not split synthetic materials on the market. In terms of properties and quality, it shows in particular the following features:

- a density that increases from the back to the front and lies between 0.50 and 1.30
- a “bloom” or a grain cracking before dressing, comparable to those in natural untanned leather,
- a “bloom” or a grain cracking after dressing, comparable to those in natural dressed leather,
- a flexibility corresponding to that of a natural untanned leather of the same thickness,
- an ability to swell again in an aqueous medium, matching that imparted by the three-dimensional structure of the collagen fibers in natural untanned leather,

- an increased porosity for air that is maintained in the material after dressing,
- a porosity for water comparable to that of natural leather, namely between 35 and 45 % after a 3-hour immersion in water under dynamic bending,
- a capacity for desorption, based on the preceding properties.

This totality of properties, which to date has never been achieved in the area of man-made leather and similar materials, makes this new material an excellent replacement for natural untanned leather in its most varied applications.

The new material is manufactured using a procedure based neither on thermo-retraction, nor requires organic solvents or the treatment of thermo-sensitization

or thermo-coagulation. The procedure according to the invention is characterized by at least one non-woven web of continuous synthetic fibers, manufactured by extrusion and that are arranged in the web without preferred orientation, with a titer between 0.5 and 10 dtex, where the value can be the same or different, being subjected sequentially to the following treatments:

- intensive needling,
- impregnation with a latex of a synthetic elastomer in emulsion or dispersion that contains a dispersible hydrophobic charge (filler) and a swelling agent with the property of later swelling again in an aqueous medium,
- drying at a temperature compatible with the nature of the fibers,
- a treatment to apply a latex of a synthetic elastomer in emulsion or dispersion that contains a hydrophobic and dispersible charge (filler) and a swelling agent with the property of later swelling again in an aqueous medium, and
- final drying at a temperature that is compatible with the nature of the fibers.

The combination of these elements, intensive needling of the web and introduction of fillers into the latex and a swelling agent, allows attaining the desired density in the material, while retaining its porosity. It is possible to start with not only one, but two or more webs placed next to each other, in particular, webs with threads of different titer, subjecting the composite to needling. Working in this manner, it is possible to achieve an even higher multidirectional stability.

However, only the choice of latex, the filler material and the swelling agent determine the appearance and the physical behavior of the material, in particular its ability to swell during dressing. The sequential treatments of impregnation and

the application of a layer determine the nature of the density from back to front that can be observed in the end product.

The implementation of the invention is elucidated in detail below, showing also the preferred forms of implementation: the continuous synthetic threads forming the basic web or webs are obtained by extrusion. They preferably consist of homopolymers or mixtures of homopolymers, or of copolymers of polyolefins, polyamides or polyesters, for instance polyethylene terephthalate. Threads of isotactic polypropylene can be used to advantage. The titer of the threads, which lies between 0.5 and 10 dtex, can for instance be of 1 to 5 dtex. If two or several webs placed next to each other are used as a starting point, then the threads of these webs can in particular have different titers in each web, with the consequence that the support's resistance to tearing improves.

In general terms, the manufacture of non-woven webs consists in extruding a polymer of the type mentioned above on an extruder. The extrudate is then pressed through a series of nozzles of a certain profile. The threads are then stretched in suitable nozzles, supported by compressed air and blown onto a formation table with the aid of a system of separators. The arrangement of these threads forms a web in which the threads are randomly arranged, in a non-parallel manner.

This web can either be needled directly, or first be transported to a folding

device, where it is then arranged in several layers, prior to needling. The weight of the web is preferably of between 100 g/m^2 and 1,000 g/m^2.

Needling should be intensive. Preferably, several passes through the needling machine will accomplish this, such that maximum randomization of the threads is achieved without destroying their continuous structure. To this end it is advantageous to first apply a sizing, which can be based on a modified or emulsifiable mineral oil.

Needling can either be performed on a web pre-needled at the exit of thread formation, or on a web obtained by folding and needling, or on an arrangement of two or more webs. To this end, a needled web at its exit from thread formation can be joined with a folded or needled web, where this type of arrangement allows destroying practically completely any preferred orientation of the threads, which makes possible achieving a support with a very strongly increased multi-dimensional stability.

If desired, at this stage it is also possible to introduce a grid or a netting in the course of bringing two webs together, with the purpose of reinforcing the

dimensional stability of the finished support. The texture of the grid is chosen in such a way that it endures the subsequent operational steps of needling/

The web so obtained is next impregnated with the latex of a synthetic elastomer in emulsion or dispersion, preferably an aqueous latex. This latex is chosen from

among the set of synthetic elastomers. We shall mention in particular latices of the acrylic type and its copolymerides, of the vinyl type and its copolymerides, of polyurethane type in dispersion, or of the type of copolymers of styrene and butadiene. It is advantageous to use a latex that yields a flexible film after application and drying.

In addition to the latex, the impregnation bath comprises a filler and a swelling agent. The purpose in adding these constituents is on the one hand, to increase the final density of the material and improving its final grindability and on the other, to reproduce the swelling capacity of natural leather in an aqueous medium, during the course of dressing. The filler can in particular consist of inorganic compounds, such as kaolin, crystallized calcium carbonate or any other readily dispersible or easily distributed mineral compound, with the proviso that it be hydrophobic in nature, which reduces the hydrophilic nature of the end material. The filler is used in amounts that preferably lie between 10 and 150 wt.-%, relative to the weight of latex dry solids. In the case of the swelling agent – which incidentally simultaneously acts as a thickener – it is in principle not important which natural or synthetic product is used, provided it swells and after drying, is able to swell again in water or an aqueous medium. The choice is made particularly among products of the carboxylmethyl-cellulose, hydroxy-methyl-cellulose or the rubber type.

The three compounds mentioned are combined in an emulsion or dispersion that is preferably aqueous and together constitute the impregnation bath, or the impregnation composition.

It should be pointed out that impregnation can not be performed only in a bath, but also by applying the composition on the web by coating, preferably using a foulard. This kind of impregnation has the effect of increasing the density gradient from one side of the web to the other, in particular if sufficient pressure is applied at the foulard. The relative amounts of the compounds and of water, i.e., the concentration of the bath or the composition, and the squeezing out that ends this operational step, are preferably such that the web retains 50 to 300 % of its weight in dry impregnation product, after the drying that follows. To this end it is important that drying be performed at a temperature compatible with the nature of the threads.

The material so obtained is then subjected to a treatment to apply a thin layer to the side to be buffed and to receive the final dressing for natural leather. Application of this layer can be accomplished by means of traditional working methods, such as with a blade, or by application using a foulard. In general, the composition for the formation of this layer, in the form of an emulsion or dispersion that is preferably aqueous, comprises compounds of a nature comparable to that described earlier for the impregnation bath and that has the same functions.

The latex of synthetic elastomers used is hence of acrylic type or its copolymers, of vinyl type or its copolymers, of the polyurethane type in dispersion, or of the type of copolymers of styrene and butadiene, without however excluding latices of a different chemical nature. It is advantageous to choose a latex in aqueous

emulsion, which after application and drying yields a harder or more rigid film than that used for impregnation, to obtain a material that on one side has a surface with maximum grindability. The term “acrylic type” means polymers of acrylic acid and its derivatives, such as acrylonitrile and acrylic esters and naturally also includes the corresponding methacrylic compounds.

With the same goal of facilitating the final process of buffing, a filler is added, in amounts of preferably 10 to 300 wt.-%, relative to dry latex solids. If necessary, a dispersant is added to the filler, for instance sodium hexametaphosphate. The filler can in particular consist of inorganic compounds that are readily dispersible and of hydrophobic nature, for instance kaolin, or crystallized calcium carbonate rendered hydrophobic.

In addition, a swelling agent is added to the composition for layer formation, which simultaneously acts as a thickener and can be the same natural or synthetic product used for impregnation and that swells in water or an aqueous medium. In particular, it is chosen from among products of the type of carboxy-methyl-cellulose, hydroxymethyl-cellulose and rubber types.

The properties of the compounds that form the aqueous emulsion or dispersion and the working method used to apply the thin layer are preferably such that the amount of the deposited dry product lies between 100 and 500 g/m^2 after final drying. Finally, it must be ensured that drying is performed at a temperature that is compatible with the nature of the threads.

The material so obtained has a thickness of preferably between 1 and 3 mm. It can then be subjected to buffing by the classic methods of tanning and to the

usual treatments for natural leather and in particular, dressing according to traditional tanning methods.

The following examples elucidate the invention.

Example 1

In a single-screw extruder, melt polypropylene at approximately 270 °C. The flowability index of the polymers i^2 230 is 15 (this index is determined by the weight of the material at 230 °C that in 10 minutes flows out of a nozzle of 2.095 mm diameter and 8 mm length, under a 2,16 kg load). The molten mass is then pressed through a system of filters and then sent to the spinning nozzles using gear pumps. The spinning nozzles have 108 holes, divided into several zones. The threads, cooled by a conditioned air system, are taken up by stretching nozzles, where they are stretched using 20 kg/cm^2. The threads are then sent by pipes to the formation table. These pipes end in a system of separators, the profile of which is so chosen that they bring about a good distribution of the threads on the table.

The properties of the threads obtained are the following:

flowability index i^2 190: 12 (this index is determined in the same manner as index i^2 230, but at 190 °C).
Titer: 2.1 dtex
Strength per norm G07-008: 3.2 g/dtex
Fracture strain per norm G07-008: 165 %

By depositing the threads on the formation table, a 150 g/m^2 web is obtained that is needled the first time with 20 punctures per cm^2. This web is then dressed and finally needled for a second time, at 100 punctures/cm^2. Next two webs of this kind are joined, which is accomplished by 4 passes through the needling machine with 125 punctures/cm^2 in each case and this, alternatively on each side. The weight of the web so obtained was 330 g/m^2.

The web obtained is then impregnated in a bath of the following composition:

- 14 % dry substance in styrene-butadiene capable of crosslinking (40:60), with a surface tension between 32 and 39 dyn/cm;
- 10 % dry substance in styrene-butadiene capable of crosslinking (65:35), with a surface tension between 32 and 39 dyn/cm;
- 18 % of hydrophobic, crystallized calcium carbonate of a grain size (granulometry) of 10 µm;
- 57 % water
- 1 % carboxylmethyl-cellulose.

Squeezing through the foulard is controlled in such a way that a deposition of dry product of 170 % is obtained, relative to the weight of the web used. Dry on a frame at 130 °C.

The subsequent coating treatment is performed using the following composition:

25 % dry substance of a homopolymers of methyl methacrylate in aqueous emulsion,
20 % hydrophobic kaolin, particle size (granulometry) of 5 µm,

53 % water,
2 % hydroxymethyl-cellulose.

Coating is accomplished by application on a foulard, where the machine is adjusted in such a way that 300 g/m^2 of dry product are deposited.

After this process step, the support is buffed on a tannery buffing machine of the Turner type that has a dedusting system. The buffed side then receives a dressing as with leather; two napping board applications are used. After each application, the support is smoothed under a static pressure at 80 °C, with a smooth sheet. Then a covering layer is applied with a spray gun, then a cellulose fixative; the assembly is napped under pressure and finally a second fixative treatment is applied.

<u>Formulation of the napping board application</u>

Pigments	200 parts
Crosslinking acrylonitrile copolymer in aqueous emulsion with 45 % dry substance	250 parts
synthetic casein	50 parts

<u>Formulation of the covering application</u>

Pigments	200 parts
Crosslinking acrylonitrile copolymer in aqueous emulsion with 45 % dry substance	250 parts
synthetic casein	50 parts
Water	500 parts

The material so obtained shows all the characteristics of leather destined for applications such as morocco leather, or in the manufacture of leather bags.

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Example 2

In the method described in Example 1, a 150 g/m^2 web is built on the formation table that is first needled at 20 punctures/cm^2 and then a second time after applying a sizing, at 100 punctures/cm^2. In the same manner, a 20 g/m^2 web is built on the formation table and hot-sealed on the piston cylinders using a calendar at 110 °C, under a pressure of 20 kg. This web is then sized folded eight times and needled on a folding needle device at 150 punctures/cm^2. The joining of the two webs mentioned is performed under the same conditions as in Example 1. The web obtained has a weight of 350 g/m^2.

Impregnation is performed using the following bath:

- 33 % dry substance in styrene-butadiene capable of crosslinking (50:50), with a surface tension between 32 and 39 dyn/cm;
- 22 % of hydrophobic, crystallized calcium carbonate of a grain size (granulometry) of 10 µm;
- 44.5 % water
- 0.5 % carboxylmethyl-cellulose.

The deposited amount is 160 % dry substance, relative to the weight of the web used. Drying is performed at 130 °C.

A layer is then applied using a foulard; its compositions is the following:

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- 30 % dry substance in styrene-butadiene capable of crosslinking (65:35), with a surface tension between 32 and 39 dyn/cm;
- 20 % of hydrophobic, crystallized calcium carbonate of a grain size (granulometry) below 5 µm;
- 47.5 % water
- 2.5 % carboxylmethyl-cellulose.

The blade is adjusted such that 400 g dry product are deposited per m^2. Dry at 130 °C.

The topside is then buffed, covered with the material described earlier in Example 1 and then receives the same dressing. The fact that a relatively rigid layer is applied prior to buffing allows achieving a very smooth upper side in this procedural step, which makes it possible to obtain a plain dressing, or a surface with only little graining. On the other hand, a very good correction of the “bloom”

is obtained, which in combination with excellent stability in all directions, achieved by superposition of the webs, makes it possible to contemplate other application areas, such as footwear.

Example 3

In a single-screw extruder, melt polyethylene terephthalate at 280 °C. The relative viscosity of the polymer is 1.63 (viscosity measured in a 50:50 mixture of phenol and tetrachloro-ethane). The molten mass is the pressed through a system of filters and then sent to spinning nozzles using a gear pump. The spinning nozzles have 108 holes divided into several zones. The threads, cooled by a system of conditioned air are then taken up by stretching nozzles, where they are stretched with 20 kg/cm^2. The threads are then sent through pipes to the formation table. These pipes end in a system of separators with a profile chosen in such a way that a good distribution of the threads on the formation table is ensured.

The properties of the threads obtained are the following:

Titer: 2.7 dtex
Strength per norm G07-008: 4.2 g/dtex
Fracture strain per norm G07-008: 125 %

By depositing the threads on the formation table, a 20 g/m^2 web is obtained, which is hot-sealed on the piston cylinder using a calendar at 150 °C and a pressure of 20 kg. This web is folded eight times, sized and needled at 150 punctures/cm^2. Two of the webs obtained in this manner are joined by placing a nylon reinforcing grid between them that has a mash width of 4 warp and 4 woof threads/cm and imparts increased stability in all directions to the support. Joining is accomplishes under the same conditions described earlier in Examples 1 and 2.

Next, impregnate with a bath of the following composition:

- 24 % butadiene-acrylonitrile latex
- 16 % hydrophobic, crystallized calcium carbonate with a grain size (granulation) of 10 µm,
- 59 % water,
- 1 % carboxylmethyl-cellulose

The amount deposited is of 200 % dry substance, relative to the weight of the web used. Drying was performed at 180 °C.

A layer of the following composition is then applied:

- 34 % dry substance in styrene-butadiene capable of crosslinking (50:50), with a surface tension between 32 and 39 dyn/cm;
- 25 % of hydrophobic, crystallized calcium carbonate of a grain size (granulometry) of 5 µm;
- 39 % water
- 2 % carboxylmethyl-cellulose.

The blade is so adjusted that 400 g dry product per m^2 are deposited. Drying takes place at 180 °C.

The support can be dressed as described earlier, i.e., by buffing and covering color dressing as for leather. The material so obtained has increased mechanical strength (tear resistance above 150 kg in every direction, in accordance with norm NF G 07-001). This allows in particular its use as replacement for very resistant leather, as used for sports articles (balls and such).

Example 4

In the manner described in Example 2, form a 20 g/m^2 web on the formation table, with threads of a titer of 2.1 dtex, which is hot-sealed on the piston cylinder using a calendar at 110 °C, under a pressure of 20 kg. Under the same conditions, but using spinning nozzles with 67 holes, form another 20 g/m^2 web, which is hot-sealed on the piston cylinder at 110 °C under a pressure of 20 kg. The threads of this web have the following properties:

- Flowability index i^2 190: 9 (this index is determined in the same manner as the index i^2 230, but at 190 °C)
- Titer: 7.3 dtex

- Strength: 2.9 g/dtex) per norm G 07-008
- Breaking tension: 200 %)

These two webs are simultaneously sent to a folding machine, joined, folded eight times, sized and then needled at 150 punctures/cm^2. The web so obtained had a weight of 320 g/m^2. It is then needled for a second time at 150 punctures/cm^2, on each side. The web obtained is impregnated on a coating facility, where the pressure applied through the foulard is such that it causes penetration through the entire thickness of the material and thus, total impregnation. This type of impregnation has the effect of increasing the density gradient, which increases from the inside of the non-woven web. The

impregnation composition is pressed through one side of the non-woven goods and because of the filtering properties of the latter, the filler is distributed mostly on or under this side.

The impregnation composition formulation was the following:

- 28 % dry substance of a self-crosslinking acrylic polymer (methyl methacrylate),
- 28 % hydrophobic, crystallized calcium carbonate with a particle size (granulometry) of 10 µm,
- 47 % water,
- 1 % carboxylmethyl-cellulose.

Application is controlled in such a way that a deposit of 200 % dry substance is obtained, relative to the weight of the web used. Dry at 140 °C in a drying cylinder. Then a layer with a composition according to the following formulation is applied on the compacted side of the material obtained:

- 20 % dry substance of an acrylic polymer (ethyl methacrylate)
- 33 % hydrophobic, crystallized calcium carbonate of a particle size (granulometry) of 40 µm,
- 46 % water that contains 10 g/L sodium hexametaphosphate,
- 1 % carboxylmethyl-cellulose.

The machine is so adjusted that 300 g/m^2 are deposited. Dry, buff and dress as described in Example 1. After buffing, the material so obtained has a smoother surface because of the presence of the filler of relatively large particle size on the surface, which has the effect of closing the structure.

Joining the webs of threads of respectively 2.1 and 7.3 dtex makes it possible to obtain a material with greater tear resistance while retaining good regularity.

The norms NF G 07-001 and G 07-008 are issued by the Association française de normalisation (AFNOR), Tour Europe, 92 Courbevoie (France).

Patent claims

1. Replacement material for natural untanned leather with a dispersible filler and a latex of a synthetic elastomer, which forms the bonding agent for at least one web based on a non-woven needled fabric of continuous synthetic threads arranged in the web without a preferred orientation, **characterized by** the dispersible filler being of a hydrophobic nature, the needled web being formed of threads with a titer of between 0.5 and 10 dtex, the value of which can be the same or different, and by the bonding agent mixture also including a swelling agent, which after drying can swell again in aqueous media, and by the bonding agent mixture being distributed inside the web in such a manner by imparting a density to it that increases from the back or left side towards the front or right side, and by this composition and this structure endowing the material with properties similar to those of natural untanned leather, allowing the same dressing, in particular dressing with products in emulsion, using a napping board or a spray gun.

2. Replacement material according to claim 1, **characterized by** the threads consisting of thread-forming homopolymers, mixtures of homopolymers, or copolymers of polyolefins, polyesters or polyamides 6 or 6/6, preferably of isotactic polypropylene.

3. Replacement material according to claim 1 or 2, **characterized by** the latex it contains being of the type of acrylic acid esters and its copolymers, vinyl esters or its copolymers, of the polyurethane type in dispersion, or of the type of copolymers of styrene and butadiene, or butadiene and acrylonitrile.

4. Replacement material according to one of the claims 1 through 3, **characterized by** the dispersible, hydrophobic filler consisting of an inorganic compound, in particular of hydrophobic kaolin or crystallized calcium carbonate.

5. Replacement material according to one of the claims 1 through 4, **characterized by** the swelling agent being of the type of carboxylmethyl-cellulose or hydroxymethyl-cellulose, the 2 % solution at 20 °C of which has a viscosity of approximately 15,000 cps, or is a vegetable rubber.

6. Procedure for the manufacture of a replacement material for natural

untanned leather according to claims 1 through 5 without using thermo-retraction, **characteriz d by** sequentially subjecting at least one non-woven web of continuous synthetic threads, obtained by extrusion, which are arranged in the web without preferred orientation, with a titer between 0.5 and 10 dtex, and which can be the same or different, to the following treatments:

- intensive needling,
- impregnation with a latex of a synthetic elastomer in emulsion or dispersion that contains a dispersible hydrophobic filler and a swelling agent with the property of later swelling again in an aqueous medium,

- drying at a temperature compatible with the nature of the threads,
- applying a layer with a latex of a synthetic elastomer in emulsion or dispersion that contains a hydrophobic, dispersible filler and a swelling agent with the property of later swelling again in an aqueous medium, and
- final drying at a temperature compatible with the nature of the threads.

7. Procedure according to claim 6, **characterized by** the concentration of the impregnation bath, or the impregnation bath composition, and the squeezing being such that after subsequent drying, the web has incorporated 50 to 300 % of its weight in dry impregnation product.

8. Procedure according to claim 6, **characterized by** the treatment to apply the thin layer being carried out in such a way that the amount of deposited dry material after final drying lies between 100 and 500 g/m^2.